OPTIMIZATION OF BIODIESEL PRODUCTION FROM COOKING PALM OIL USING RESPONSE SURFACE METHODOLOGY (RSM) APPROACES

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering in Biotechnology

Faculty of Chemical and Natural Resources Engineering
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JULY 2012

ABSTRACT

Biodiesel is one of the renewable energy resource which is suitable to replace the fossil fuel due to the depletion of fossil fuel in the future. The modeling of the design of experiment for optimization of biodiesel production from cooking palm oil is conducted by using Design Expert software version 7.1.6 (Stat Ease). This experimental design is conducted in order to optimize the biodiesel production with significant parameters that affecting the biodiesel production. The parameters that have been used are reaction temperature, methanol to oil molar ratio, catalyst concentration and reaction time. By using response surface methodology (RSM), the optimal parameters levels are determined. The optimum conditions for biodiesel production were at temperature of 72.83°C, alcohol to oil molar ratio of 9.5:1, 3.95% of catalyst concentration and 4.73 hours of reaction time, which was obtained 88.38% of biodiesel yield.

ABSTRAK

Biodiesel merupakan salah satu daripada sumber yang boleh diperbaharui amat sesuai dijadikan bahan ganti kepada sumber galian. Perisian Design Expert versi 7.1.6 (Stat Ease) digunakan bagi merangka model penghasilan biodiesel daripada minyak masak diperbuat daripada kelapa sawit pada tahap optimum. Objektif eksperimen ini adalah untuk memaksimakan penghasilan biodiesel di bawah pengaruh parameter-parameter penting yang memberi impak terhadap penghasilan biodiesel. Parameter yang digunakan adalah suhu tindakbalas, kepekatan pemangkin, nisbah molar methanol terhadap minyak dan masa tindakbalas. Dengan menggunakan 'response surface methodology' dari perisian 'Design Expert', tahap optima setiap parameter dapat ditentukan. Optimum kondisi bagi penghasilan biodiesel adalah pada suhu 72.83°C, nisbah molar menghampiri 9.5:1, 3.95% daripada kepekatan pemangkin dan tindakbalas menggambil masa selama 4.73 jam dengan menghasilkan biodiesel sebanyak 88.38%.

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LIST OF SYMBOLS

%	Percentage
°C	Degree celcius
+α	High alpha point
-α	low alpha point
Y	biodiesel yield
X_1	Reaction temperature
X_2	Molar ratio
X_3	Catalyst concentration
X_4	Reaction time

LIST OF ABBREVIATIONS

DoE	Design of Experiment
FAME	Fatty acid methyl ester
WCO	World Customer Organization
wt%	weight percent
SO_2	Sulphur dioxide
CO_2	Carbon dioxide
CO	Carbon monoxide
CaO	Calcium oxide
$Ca(OH)_2$	Calcium hydroxide
$CaCO_3$	Calcium carbonate
KOH	Potassium hydroxide
FFA	Free fatty acid
NaOH	Sodium hydroxide
ZnO	Zinc oxide
et al	and other
CCD	Composite central design
ANOVA	Analysis of variance
Inc.	Incorporation
w/w%	Weight per weight percent
w/w_{oil}	Weight per weight oil
RSM	Response surface methodology
GC	Gas chromatography
GC-MS	Gas chromatography mass spectroscopy

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

In last few years, worldwide energy demand increase significantly due to the needs from development of global economics and population growth (El Boulifi,N. *et al.*, 2010). There are many type of energy that uses by the global economics and population growth which are fossil energy, nuclear energy, hydroelectricity and others energy resources.

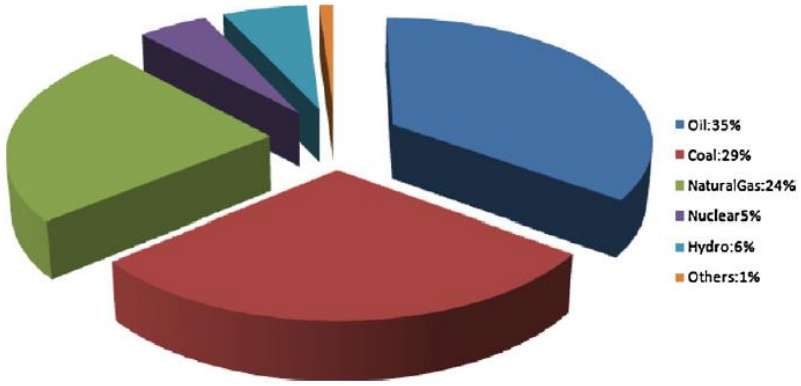

Figure 1.1: World Primary Energy Production in 2009 (Lin L. *et al.*, 2011)

Figure 1 shown that fossil fuels is the major fuel with 88% of world primary energy consumption that include oil (35%), coal (29%) and natural gas (24%) while nuclear energy and hydroelectricity accounted as 5% and 6% of the total primary energy consumption (Lin lin et al., 2011). Primary energy is defined as essentially raw energy which has not been subjected to any transformation or conversion process and includes

natural fossil fuels and renewable energy (Steven L. and Lee K. T., 2010). Economic growth and population growth are the main factors of the growing global energydemand. Actually, there is a link between energy demand and economic output. On average, the global economy is projected to grow by 3.1% a year to 2020. Currently, world population is growing at an annual rate of 1.4% per year where the population growth among the 4.8 billion people living in the developing countries is 1.7% per annum with additional 81 million mouths to feed annually. This compares with an average 0.3% per annum in the developed countries which means that the share of the world population living in developing countries will raise from 77 today to 81% in 2020. In view of these trends, access is provide to commercial energy in developing countries will be an increasingly large and urgent challenge (Mamdouh G. S., 2003).

1.2 PROBLEM STATEMENT

The most growing global energy demands currently are the fossil energy sources. The problem is fossil energy resources are non-renewable, which are limited in supply and will be depleted one day (El Boulifi,N. *et al.*, 2010). Fossil fuels need millions of years to be formed from natural resources which are the fossilized remains of dead plants and animals by exposure to heat and pressure in the Earth's crust over millions of years. Because of that, fossil fuels have been categories as a non-renewable resource which is cannot be renew for the next uses. The world energy demands increase everyday make the researcher to develop another energy resource that can be renewable such as biodiesel.

The researchers and scientific community worldwide nowadays have focused on the development of biofuels, which is biodiesel, and the process of optimization to meet the standard and specifications needed in order for fuels to use commercially without compromising on the durability of the engine parts (Sharma,Y. C. *et al.*, 2008). The major issue towards widespread commercialization is the high price of biodiesel (Refaat,A. A. et al., 2007). Biodiesel is expensive because of the high price of the plant oil and some issues on the processing technologies such as the catalyst and equipment (Xin D.*et al.*, 2010).

The option in this study to reduce the price of the biodiesel is by optimize the production of biodiesel. But, it is difficult to study this optimization using classical method because a lot of parameters can affected this biodiesel production. In order to solve this problem, this study was carried out by using design of experiment (DoE) due to the ability to optimize the response with multiple variables involved.

1.3 RESEARCH OBJECTIVE

The main objective in this study is;

i. To optimize the biodiesel production using design of experiement (DoE) approaches.

1.4 SCOPE OF STUDY

To achieve the objective of this research, three scopes have been identified:

i. To optimize the biodiesel production by using design of experiment (DoE) with different of parameters (reaction time, reaction temperature, catalyst concentration and methanol to oil molar ratio).
ii. To identify the characteristics of fatty acid methyl esters (FAME) using gas chromatography.

1.5 RATIONAL AND SIGNIFICANCE

The finding on this study will provide the optimum conditions to carry out the transesterification process in order to maximize the biodiesel yield. With the highest biodiesel yield produced from transesterification process will reduce the production cost. Therefore, biodiesel can be commercialized as a biofuel especially for transportation usage.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

Biodiesel is clean burning alternative fuel renewable resources that produced from domestic and contained no petroleum (Stalin,N. and Prabhu,H. J., 2007). Biodiesel, generally known as fatty acid methyl ester (FAME), is derived vegetable oils or animal fats produced by process of transesterification in which, oil is reacted with monohydric alcohol in presence of a catalyst (AshishK.,*et al.*, 2010). Biodiesel has been defined by World Customer Organization (WCO) as "*a mixture of mono-alkyl esters of long-chain (C16-18) fatty acids derived from vegetable oils or animal fats which is a domestic fuel for biodiesel engines and which meets the specifications of ASIM D6751*."

Biodiesel is much better than conventional diesel in terms of its flash point, sulphur content and aromatic content. The biodiesel essentially non-aromatic and sulphur free meanwhile conventional diesel can contain up to 500 ppm SO_2 and from 20 to 40 wt% aromatic compounds. These advantages will help reducing of urban pollution. Vehicle that used diesel as a fuel will produce black smoke and contribute to one third of the total transport that generated greenhouse gas because of the diesel is dominant for black smoke particulate together with SO_2 emissions. But by using biodiesel, it will decrease an average of 14% for CO_2, 17.1% for CO and 22.5% for smoke density (Anh, N. P. and Tan, M. P., 2008). Another advantages are bio-degradable, non-toxic in nature, has low emission profile that helps reducing global warming and hence eco-friendly (Banerjee, A. and Chakraborty, R., 2009).

2.1 COMPOSITION OF VEGETABLE OILS AND FATS

Animal fats and vegetable oils usually have hydrophobic properties that make them insoluble in water. Vegetable oils and animal fats consists triglycerides that will derived into biodiesel in the chemical reaction. Both 1 mol glycerol and 3 mol fatty acids combine to build up triglycerides. Fatty acids vary in terms of the length of carbon chain and number of unsaturated bonds. The chemical structure of common fatty acids is shown in Table 2.1. The saturated fatty acids consist of no double bond while the unsaturated fatty acids consist of double bonds. The saturated chains contain maximum number of possible hydrogen atoms per atom carbon. Meanwhile, unsaturated chains do not contain maximum number of possible hydrogen atoms because of the presence of double bond(s) in some carbon atoms. Natural vegetable oils and animal fats can be obtained through mechanical pressing or solvent extraction in the crude form and containing a lot of impurities such as sterol, free fatty acid and water. These free fatty acids and water content will significantly give an effect to transesterification reaction especially if it use base as catalyst. The presence of water content can reduce the yield of methyl esters. Particularly at high temperature, in the presence of water, it can hydrolyze triglycerides to diglycerides and form free fatty acid. Hydrolysis reaction has shown in Figure 2.2. These free fatty acids will subsequently react to form soap in the presence of base catalyst as shown in Figure 2.1. The formation of soap can interfere with the separation of fatty acid methyl ester (FAME) and glycerol during water washing (purification) process. (Man K. L. *et al.*, 2010).

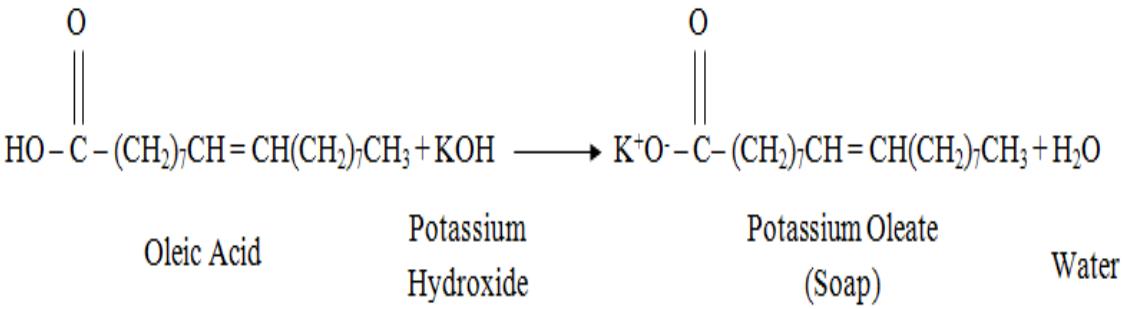

Figure 2.1: Formation of soap from reaction of free fatty acid and base catalyst

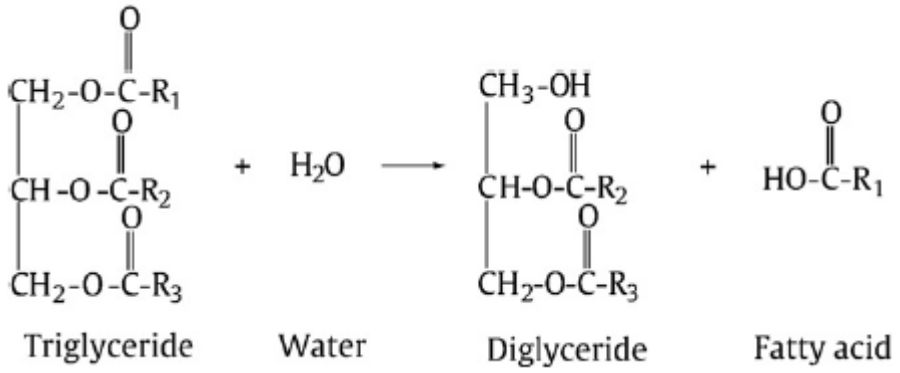

Figure 2.2: Hydrolysis reaction

Table 2.1: Chemical structure of common free fatty acids

Name of Fatty Acid	Chemical Name of Fatty Acids	Structure (xx:y)	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Oleic cis-9-	Octadecanoic	18:1	$C_{18}H_{34}O_2$
Linoleic cis-9,cis-	Octadecadienoic	18:2	$C_{18}H_{32}O_2$
12-	cis-9,cis-12,cis-15-	18:3	$C_{18}H_{30}O_2$
Linolenic	Octadecatrienoic	20:0	$C_{20}H_{40}O_2$
Arachidic	Eicosanoic	22:0	$C_{22}H_{44}O_2$
Behenic	Docosanoic	22:1	$C_{22}H_{42}O_2$
Erucle	cis-13-Docosenoic	24:0	$C_{24}H_{48}O_2$
Lignoceric	Tetracosanoic		

Source: S. P. Singh and Dipti Singh, 2009

2.2 BIODIESEL COMPOSITION

Biodiesel is a mixture of fatty acid alkyl esters that produced by using alcohol as a reactant. However, methanol is widely used because of its availability and low cost. Production of biodiesel will have different composition of FAME due to the different used of feedstock. Table 2.2 show a FAME composition that commonly found in biodiesel (Man K. L. *et al.,* 2010)

Table 2.2: Common composition of FAME

Methyl Ester	Formula	Common Acronym	Molecular Weight
Methyl palmitic	$C_{17}H_{34}O_2$	C16:0	270.46
Methyl stearate	$C_{19}H_{38}O_2$	C18:0	298.51
Methyl oleate	$C_{19}H_{36}O_2$	C18:1	296.50
Methyl linoleate	$C_{19}H_{34}O_2$	C18:2	294.48
Methyl linolenate	$C_{19}H_{24}O_2$	C18:3	292.46

Source: Man K. L. *et al.*, 2010

2.3 BIODIESEL DERIVATION TECHNIQUE

It is not possible to use directly from vegetable oils and animal fats as combustible fuel is not suitable due to their high kinematic viscosity and low volatility. It can posed serious problem in their long terms used such as deposition, ring sticking and injector chocking in the engine. To overcome this problem, the vegetable oils and animal fats must be subjected to chemical reaction in order to reduce the viscosity of the oils (Man K. L.*et al.*, 2010). The problems, causes and potential solutions for directly use vegetable oils in diesel shown in Table 2.4.

There are 5 techniques that used in this derivation which are dilution, micro-emulsion, pyrolysis, antransesterification modification techniques and supercritical methanol. Micro-emulsion is a technique where are using with an additional of alcohols that have been prepared to overcome the problem of high viscosity of vegetable oils. Pyrolysis is a cleavage to smaller molecules by thermal energy, of vegetable oils over catalyst. The most famous technique that has used in biodiesel processing technologies is transesterification technique (Amish P. V.*et al.*, 2010). In that technique, the triglycerides are converted into fatty acid methyl ester (FAME) with glycerol as byproduct in the presence of short chain alcohol, such as methanol, and catalyst, such as alkali or acid. Figure 2.3 has shown a general equation of transesterification reaction. Table 2.3 has summarized the advantages and disadvantages of each technique.

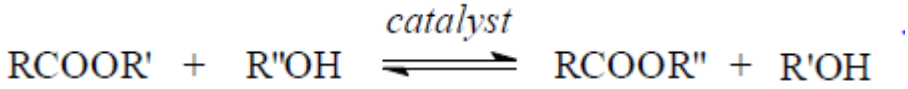

Figure 2.3: General equation of transesterification reaction

Table 2.3: Comparison of advantages and disadvantages between techniques

Technique	Advantage	Disadvantage
Dilution / micro-emulsion	• Simple process	• High viscosity • Bad volatility • Bad stability
Pyrolysis	• Simple process • No polluting	• High temperature is required • Equipment is expensive • Lowpurity
Tranesterification	• Fuel properties is closer to biodiesel • High conversion efficiency • Low cost • It is suitable for industrial production	• Low free fatty acid and water content are required (for base catalyst) • Pollutants will be produced because products must be neutralized and washed • Accompanied by side reactions • Difficult reaction products reaction
Supercritical methanol	• No catalyst • Short reaction time • High conversion • Good adaptability	• High temperature and pressure required • Equipment cost is high • High energy consumption

Source: Lin *et al.*, 2011

Table 2.4: Problems, causes and potential solutions for directly use vegetable oils in diesel

Problem	Cause	Potential Solution
Short term		
1. Cold weather starting.	High viscosity, low cetane, and low flash point of vegetable oils.	Pre-heat fuel prior to injection. Chemically alter fuel to an ester.
2. Plugging and gumming of filters, lines and injectors.	Natural gums (phosphatides) in vegetable oil. Other ash.	Partially refine the oil to remove gums. Filter to 4 μm.
3. Engine knocking.	Very low cetane of some oils, improper injection timing.	Adjust injection timing. Use higher compression engines. Pre-heat fuel prior to injection. Chemically alter to an ester.
Long term		
4. Coking of injectors on piston and head of engine.	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils.	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to anester.
5. Carbon deposits on piston and head of engine.	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils.	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester.
6. Excessive engine wear.	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil.	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation.
7. Failure of engine lubricating oil due to polymerization.	Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs.	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation.

Source: Mustafa B. and Havva B.(2008)

2.4 TRANSESTERIFICATION

Transesterification is an equilibrium reaction and it occurs essentially by mixing of two reactants (fatty acid methyl ester and alcohol). The adjustment of the equilibrium can accelerate by applying the presence of catalyst on the reaction typically either a strong acid or base (Ulf S.*et al.*, 1998). Three common kinds of catalysts that use in this process are lipase catalyst, acid catalyst, and base or alkali catalyst (Lin L.*et al.*, 2010).

2.5 ALKALI CATALIZED TRANSESTERIFICATION

A base-catalyzed transesterification process is normally use in biodiesel production because alkaline metal alkoxides and hydroxide are more effective than acid catalyst (Yusuke A.*et al.*, 2009). The speed of base-catalyzed transesterification process is higher than using acid catalyst. However, these types of transesterification process are very sensitive to the presence of water and free fatty acids and also needs a lot of alcohols in its reaction (Lin L.*et al.*, 2010). Figure 2.4 has shown the mechanism of the base catalyst transesterification.

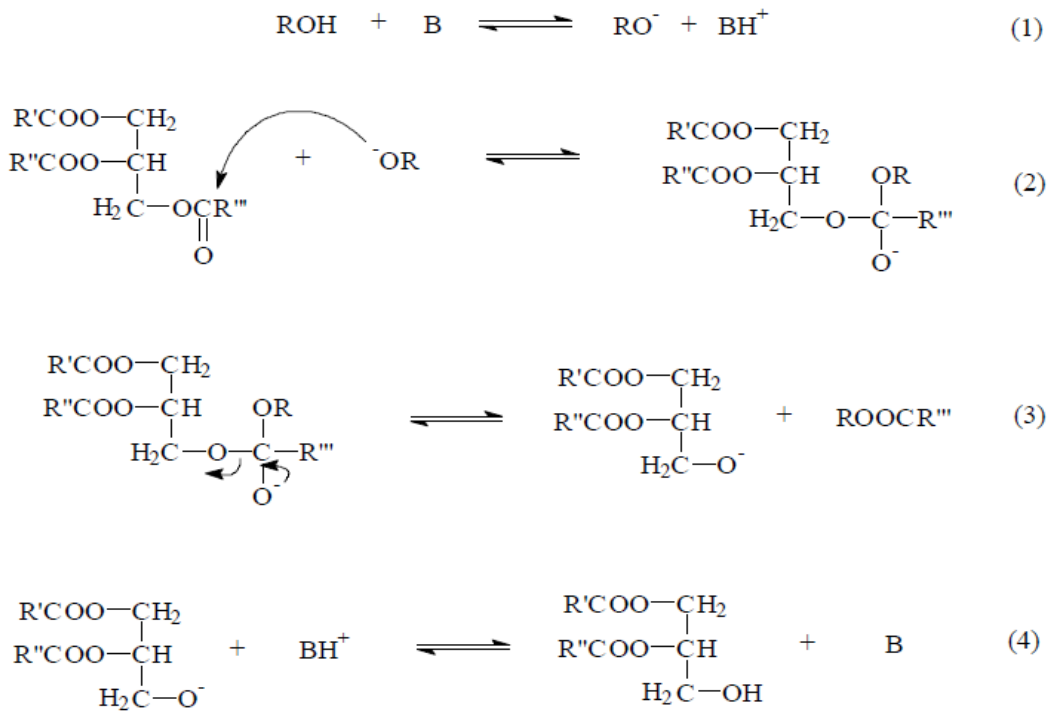

Figure 2.4: The mechanism of the base catalyst transesterification

Masato *et al.* had studied about solid base catalyst for biodiesel production with environment benignity and found that by using CaO as catalyst had yield 93% of fatty acid methyl ester in 1 hour duration time better than $Ca(OH)_2$ and $CaCO_3$. But after 2 hour of reaction time with CaO as catalyst, fatty acid methyl ester yield more than 99% but the portion of catalyst had changed into calcium soap by reacting with free fatty acids included with waste cooking oil in the initial stage of transesterification. Meher,L. C. *et al.* had found that 98% of methyl ester had yield from karanja oil by using alkaline transesterification under optimal condition which are 1% of KOH concentration, 6:1 of molar ratio, rate of mixing 360 rpm at 65˚C of reaction temperature for 3 hour period of time.

Umer R. and Farooq A. had studied the optimization of rapeseed oil through alkaline-catalyzed transesterification and they found that the best yield and quality produced are at methanol/oil molar ratio, 6:1; potassium hydroxide catalyst concentration, 1.0%; mixing intensity, 600 rpm and reaction temperature 65°C. by using calcined sodium silicate as a solid base catalyst, Feng G.*et al.* found that transesterification of soybean oil had yield almost 100% of biodiesel under optimum condition which are sodium silicate of 3.0 wt.%, a molar ratio of methanol/oil of 7.5:1, reaction time of 60 min, reaction temperature of 60°C, and stirring rate of 250 rpm.

2.6 PARAMETER STUDIES IN OPTIMIZATION PROCESS

There many parameters that used by the researchers in order to study the optimization of biodiesel production, such as agitation speed, pH, free fatty acid (FFA) content, reaction temperature, etc. Table 2.5 shows the parameters used by the researchers to optimize the biodiesel production from various feedstocks.

Table 2.5: Parameters used to optimize the biodiesel production

Feedstock	Parameter	Biodiesel Yield (%)	Reference
Crude canola oil	▪ Reaction temperature: 50°C ▪ Weight catalyst at 0.2 mol/mol: 1.59% by weight ▪ Methanol to oil molar ratio: 4.5:1	95.8	Singh *et al.*, 2006
Crude cottonseed oil	▪ Methanol to oil molar ratio: 7.9:1 ▪ Reaction temperature: 53°C ▪ Reaction time: 45 minutes ▪ Catalyst concentration: 1.0% ▪ Mixing rate: 268 rpm	97.0	Xiaohu *et al.*, 2011
Animal fats, restaurant waste oil and frying oil	▪ Amount of methanol: 40% by volume ▪ Catalyst concentration: 0.3% by weight ▪ Reaction temperature: 65°C ▪ Reaction time: 90 minutes	80	Math *et al.*, 2010
Jatropha curcas L.	▪ Methanol to oil molar ratio: 6:1 ▪ Catalyst concentration: 1% by weight ▪ Reaction temperature: 60°C ▪ Reaction time: 40 minutes	98.6	Nakpong and Wootthikanokkhan, 2010

Table 2.5:-Continued

Feedstock	Parameter	Biodiesel Yield (%)	Reference
Palm oil	▪ Reaction time: 3 hours ▪ Reaction temperature: 127°C ▪ Methanol to oil molar ratio: 8:1 ▪ Catalyst concentration: 6% by weight	83.3	Yee and Lee, 2008
Waste cooking palm oil	▪ Methanol to oil molar ratio: 29:1 ▪ Catalyst concentration: 2.7% by weight ▪ Reaction time: 87 minutes ▪ Reaction temperature: 115.5°C	79.7	Nadyaini and Aishah, 2011
Jojoba oil	▪ Catalyst concentration: 1.35% ▪ Reaction temperature: 25°C	83.5	Bouaid et al., 2007